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Effect of static Jahn-Teller distortion on magnetism in the manganite system : $La_{1-x}Sr_xMnO_3$

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Abstract : The colossal magnetoresistance manganite system is described by a simple Hamiltonian containing the hopping term arising out of the itinerant e_g electrons of Mn atom in presence of a static band Jahn-Teller lattice distortion and the external magnetic field in the same e_g band. The ferromagnetism originates due to the more localized core t_{2g} electrons. The itinerant e_g electrons are hybridized with the on-site t_{2g} electrons with a strong hybridization. The magnetization (m) and lattice strain ($\bar{e}$) are considerably influenced by the model parameters of the system : *i.e.* the t_{2g} level (d), hybridization (v), magnetic coupling (g_1), J-T coupling (g), external magnetic field (b) and the impurity concentration (x). In same situations the ferromagnetic metallic state is pushed to higher temperatures. The results are discussed.

Keywords : Electron-electron interaction, magnetically ordered materials, exchange and super exchange.

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1. Introduction

Magnetic oxides show a variety of extrinsic magneto-transport phenomena. Among the magnetic oxides $Re_{1-x}A_xMnO_3$ (Re = La, Nd, Pr, Gd, A = Ca, Sr, Ba) are belived to be half metallic having only one spin sub-band at the Fermi level. These fully spin-polarised oxides have great potential for applications in spin-electronic devices and have, accordingly attracted intense research activity in recent years [1,2]. Studies were stimulated by the discovery of "colossal magneto resistance" (CMR) in ferromagnetic perovskites of the type $La_{1-x}Sr_xMnO_3$. Depending on doping these compounds show a complex magnetic phase diagram [3]. Ferromagnetism is found in the doping range $0.2 < x < 0.5$. The highest Curie temperatures are found in the archetypal compound $La_{1-x}A_xMnO_3$ at a doping level x of the order 1/3 with T_c ~270 K (Ca substitution), 360 K (Sr), 330 K (Ba).

The manganites show a metal-insulator transition accompanying the ferromagnetic transition. Ferromagnetic order in the mixed-valence manganites is induced by the double exchange mechanism proposed by Zener [4–6]. The large J_H modulates the hopping of an outer-shell electron between two Mn sites by the relative alignment of the core spins, being maximal when the core spins are parallel and minimal when they are antiparallel. Also, electron hopping promotes ferromagnetic order. This phenomenon, called double exchange [4–6], has been widely regarded [7–9] as the only significant physics in the regime $0.2 \leq x \leq 0.5$. However, it was previously shown [10–13] that double exchange alone cannot account for the very large resistivity of the $T > T_c$ phase or for the sharp drop in resistivity just below T_c, and was suggested that the necessary extra physics is a strong electron-phonon coupling due in part to a Jahn-Teller splitting of the Mn e_g states. The cubic-tetragonal phase transition observed for $0 \leq x \leq 0.2$ is known to be arising due to a frozen-in Jahn-Teller distortion. The interplay of ferromagnetism and band Jahn-Teller distortion present in e_g electrons alone in

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manganite system is investigated recently [14]. In the present model we consider the Jahn-Teller distortion in e_g states and magnetism in t_{2g} states.

2. Formalism

We consider here the itinerant *eg* electrons of Mn atoms in presence of the ferromagnetically ordered localized t_{2g} electrons. The strong Hund's rule coupling aligns the localized spins in the t_{2g} state. In the simplified model under consideration, we assume the existence of a direct Heisenberg type exchange interaction between the localized t_{2g} electrons to be responsible for their ferromagnetic state. Furthermore, calculations are performed in the mean field approximation accounting for the magnetic exchange interaction in the Ising limit. Since the e_g band is doubly degenerate a band Jahn-Teller distortion is invoked to remove the degeneracy. An external magnetic field drastically reduces the magnetic state and drives the system from insulating ferromagnetic state to a metallic ferromagnetic state. The aim of the calculation is to study the interplay between the transitions from the paramagnetic to the ferromagnetic state and the structural transition induced by the band Jahn-Teller distortion. The different terms in the model Hamiltonian are detailed below.

We consider a model system in which the e_g electrons of the Mn atoms are in a two fold degenerate band and interact with the lattice as well as between themselves.

$$H_c = \sum_{k,\sigma} (\in_0 (k) - \mu - \beta\sigma)(c^{\dagger}_{1k,\sigma} c_{1k,\sigma} + c^{\dagger}_{2k,\sigma} c_{2k,\sigma}), \quad (1)$$

where H_c represents the non-interacting electronic energy in a two-fold degenerate (e_g) band with single particle energy $\in_0(k)$ and chemical potential μ. The operators $c^{\dagger}_{\alpha k\sigma}(c_{\alpha k\sigma})$ being the creation (annihilation) operators of the electron in the band α of spin σ and energy $\in_0(k)$ (α = 1, 2; is the orbital index). Here B is the external magnetic field acting in the spin direction σ where $\sigma = +1$ for spin up and $\sigma = -1$ for spin down.

The coupling between the electron density in a degenerate electron band with static elastic strain mode is of the form

$$H_{e-L} = \sum_{k,\sigma} Ge(c^{\dagger}_{1k,\sigma} c_{1k,\sigma} + c^{\dagger}_{2k,\sigma} c_{2k,\sigma}) \quad (2)$$

where G is the strength of the electron lattice interaction in presence of a tetragonal distortion e. Therefore, the interaction of the electrons in the degenerate conduction band with the lattice acts as external perturbation to the free electrons in the band which tries to create a population difference between the two bands. As the population difference increases, the strain builds up in the system resulting in a splitting of the single degenerate band into two with band energies $\in_{1,2}(k) = \in_0(k) \pm Ge$, provided there is a net gain in the electronic energy due to the redistribution of electrons between the split sub-bands in comparison to the cost in the elastic energy.

In this approximation, the elastic energy is given by

$$H_L = \frac{5}{4}(C_{11} - C_{12})e^2. \quad (3)$$

where $(C_{11}-C_{22})$ is the elastic constant in the absence of strain which softens when the system undergoes the cubic to tetragonal transition. Under this situation there are two non-degenerate bands separated by a gap of magnitude $2Ge$ [15].

The localized core electron states of t_{2g} electrons are represented by the Hamiltonian

$$H_f = E_f \sum_{k,\sigma} f^{\dagger}_{k,\sigma} f_{k,\sigma}, \quad (4)$$

where $f^{\dagger}_{k,\sigma}(f_{k,\sigma})$ is the creation (annihilation) operator of the t_{2g} electrons in the $3d$-states of manganese atom with wave vector k and spin σ and E_f is its energy level.

The Heisenberg exchange interaction between the spins of the t_{2g} core electrons at the i-th and j-th atomic sites is given by

$$H_M = -\sum_{i \neq j} J'_{ij} \boldsymbol{S}_i . \boldsymbol{S}_j, \quad (5)$$

where the effective interaction energy $J < 0$ for antiferromagnetic and $J > 0$ for ferromagnetic exchange. This interaction in the Ising limit is written as

$$H_M = \frac{JM}{\cdot} \sum_{\alpha,k} \left[f^{\dagger}_{k\uparrow} f_{k\uparrow} - f^{\dagger}_{k\downarrow} f_{k\downarrow} \right], \quad (6)$$

where the Ferromagnetic order parameter

$M = - < S^z >$. The electron hops in the ferromagnetic metallic state. The Jahn-Teller distortion in manganite system is assumed to be larger than the crystal field splitting between the t_{2g} and e_g electron states. So the t_{2g} d-electron levels of the system hybridize with the e_g electron bands.

Since the manganite system possesse large Jahn-Teller distortion (~1 eV) the lower of the two e_g orbital is filled while the upper one remains vacant. Hence the lower e_g

orbital (*i.e.* $c_{1k\sigma}$) hybridizes with the localized t_{2g} electrons and gains some itinerant character, as a result the magnetic ordering due to the t_{2g} electron states is modified. For simplicity of calculation we consider the hybridization of the d electrons (t_{2g} state) with $c_{1k,\sigma}$ of the conduction electrons of band 1 only. The Hamiltonian H_V represents the hybridization effect and is given by

$$H_V = V\sum_{k,\sigma}(c^{\dagger}_{1k,\sigma}f_{k,\sigma} + f^{\dagger}_{k,\sigma}c_{1k,\sigma}), \tag{7}$$

where V is the momentum-independent hybridization matrix. Hence the manganite system exhibiting Jahn-Teller static lattice distortion and ferromagnetism in presence of external applied magnetic field can be described by the total Hamiltonian

$$H = H_c + H_{c\text{-}L} + H_L + H_f + H_M + H_V. \tag{8}$$

3. Calculation of magnetization *(M)* and Jahn-Teller distortion

The double time single particle electron Greens functions are calculated by equations of motion method of Zubarev [16]. The electron Greens functions are defined as

$$A(k\uparrow,\omega) = \left\langle\left\langle c_{1k,\uparrow}; c^{\dagger}_{1k,\uparrow}\right\rangle\right\rangle_{\omega}$$

$$A(k\downarrow,\omega) = \left\langle\left\langle c_{1k,\downarrow}; c^{\dagger}_{1k,\downarrow}\right\rangle\right\rangle_{\omega}$$

$$B(k\uparrow,\omega) = \left\langle\left\langle c_{2k,\uparrow}; c^{\dagger}_{2k,\uparrow}\right\rangle\right\rangle_{\omega}$$

$$B(k\downarrow,\omega) = \left\langle\left\langle c_{2k,\downarrow}; c^{\dagger}_{2k,\downarrow}\right\rangle\right\rangle_{\omega}$$

$$G(k\uparrow,\omega) = \left\langle\left\langle c_{k,\uparrow}; c^{\dagger}_{k,\uparrow}\right\rangle\right\rangle_{\omega}$$

$$G(k\downarrow,\omega) = \left\langle\left\langle c_{k,\downarrow}; c^{\dagger}_{k,\downarrow}\right\rangle\right\rangle_{\omega}. \tag{9}$$

The magnetization of the manganite system is defined as

$$M = N\tilde{\mu}(n^f_{\uparrow} - n^f_{\downarrow}), \tag{10}$$

where N, $\tilde{\mu}$ are the number of atoms per unit volume and magnetic moment of the manganese atom respectively. The number operatores $n^c_{i\sigma}$ and n^c_{σ} with i = 1,. 2 for the conduction electrons and the localized electrons respectively, are found to be

$$n^c_{1\downarrow} = \sum_k \frac{1}{\omega_{11}}\left[(\omega_1 - E_{1f})f(\beta\omega_1) - (\omega'_1 - E_{1f})f(\beta\omega'_1)\right],$$

$$n^c_{1\uparrow} = \sum_k \frac{1}{\omega_{22}}\left[(\omega_2 - E_{2f})f(\beta\omega_2) - (\omega'_2 - E_{2f})f(\beta\omega'_2)\right],$$

$$n^c_{2\uparrow} = \sum_k f(\beta\omega_3),$$

$$n^c_{2\downarrow} = \sum_k f(\beta\omega_4),$$

$$n^c_{\uparrow} = \sum_k \frac{1}{\omega_{11}}\left[(\omega_1 - e_{1k})f(\beta\omega_1) - (\omega'_1 - e_{1k})f(\beta\omega'_1)\right],$$

$$n^c_{\downarrow} = \sum_k \frac{1}{\omega_{22}}\left[(\omega_2 - e_{2k})f(\beta\omega_2) - (\omega'_2 - e_{2k})f(\beta\omega'_2)\right], \tag{11}$$

where $\omega_{11} = \omega_1 - \omega'_1$, $\omega_2 - \omega'_2$, and $\beta = (k_BT)^{-1}$ and the Fermi function in general is given by $f(y) = \dfrac{1}{e^y + 1}$. The quasi particle energies ω_j and ω'_j (with j = 1, 2) are given by

$$\omega_j = \frac{1}{2}\left[e_{jk} + E_{jf} + \sqrt{(e_{jk} - E_{jf})^2 + 4V^2}\right],$$

$$\omega'_j = \frac{1}{2}\left[e_{jk} + E_{jf} - \sqrt{(e_{jk} - E_{jf})^2 + 4V^2}\right],$$

$$\omega_3 = e_{3k},\ \omega_4 = e_{4k}, \tag{12}$$

where

$$e_{1k} = \in_0(k) - \mu - B + Ge,$$
$$e_{2k} = \in_0(k) - \mu + B + Ge,$$
$$e_{3k} = \in_0(k) - \mu - B - Ge,$$
$$e_{4k} = \in_0(k) - \mu + B - Ge,$$

$$E_{1f} = E_f + \frac{JM}{2},$$

$$E_{2f} = E_f - \frac{JM}{2}. \tag{13}$$

The strain energy is bounded and the static band Jahn-Teller distortion is found by minimizing the free energy using the total Hamiltonian given in the eqn. (8). It is given by

$$e = G\sum_{k,\sigma}\left[\left\langle c^{\dagger}_{1k,\sigma}; c_{1k,\sigma}\right\rangle - \left\langle c^{\dagger}_{2k,\sigma}; c_{2k,\sigma}\right\rangle\right]. \tag{14}$$

The chemical potential of the electron system changes with temperature (T) and the concentration of the doped impurity (x) in the system $La_{1-x}Sr_xMnO_3$. Since the impurity produces holes in the MnO_3 plane, the chemical potential (μ) is determined from the average number of electrons ($n - x$) which is given by

$$(n-x) = \sum_{k,\sigma} \left[\left\langle c^{\dagger}_{1k,\sigma}; c_{1k,\sigma} \right\rangle + \left\langle c^{\dagger}_{2k,\sigma}; c_{2k,\sigma} \right\rangle \right]. \tag{15}$$

The sum over the momenta of the electrons in the conduction band is replaced by the integration over energy of the electron $\epsilon_0(k)$ with integration $\sum_k = \int N(\epsilon_0) d\epsilon_0$. Here $N(\epsilon_0)$ is the model density of states [14, 17] and $2D$ is total band width W of the conduction band. To simulate the strong energy dependence of $N(\epsilon_0)$ around the center of the band we take

$$N(\epsilon_0) = N(0)\sqrt{1-\left|\frac{\epsilon_0}{D}\right|}\ln\left|\frac{D^2}{\epsilon_0^2}\right|, \tag{16}$$

where $N(0)$ is unperturbed density of state of the conduction electron at the Fermi level and ϵ_0 is the kinetic energy of the conduction band.

The physical quantities involved in the calculations are scaled with respect to the band energy (W) of the conduction band. The dimensionless parameters are given by

$$y = \frac{\epsilon_0(k)}{W}, \quad t = \frac{k_B T}{W}, \quad \dot{g} = \frac{G e_0}{W},$$

$$z = \frac{\mu}{W}, \quad b = \frac{B}{W}, \quad g_1 = \frac{JN\tilde{\mu}}{W},$$

$$\tilde{e} = \frac{e}{e_0}, \quad m = \frac{M}{N\tilde{\mu}}, \quad v = \frac{V}{W}, \quad d = \frac{E_f}{W}. \tag{17}$$

4. Results and discussion

In the manganite system $La_{1-x}Sr_xMnO_3$, there occurs a static elastic strain in the electron density in a degenerate e_g electron band. Due to strong Hund's rule coupling the t_{2g} electrons align ferromagnetically with Curie temperature $T_c \approx 250$ K. The lattice distortion in the form of static Jahn-Teller distortion is expected to suppress or to enhance the Curie temperature and thereby dropping the resistivity below T_c in the concentration range $0.2 \leq x \leq 0.5$. In the present communication we want to study the effect of J-T distortion on the magnetization and T_c. The dimensionless parameters involved in the calculations are the magnetization (m), lattice strain ($\tilde{e}$), lattice coupling strength (g), magnetic coupling strength (g_1), the position of the t_{2g} electron level (d), the hybridization (v) between e_g and t_{2g} electrons, chemical potential (z), impurity concentration (x) and temperature (t). The magnetization (m) in eqn. (10),

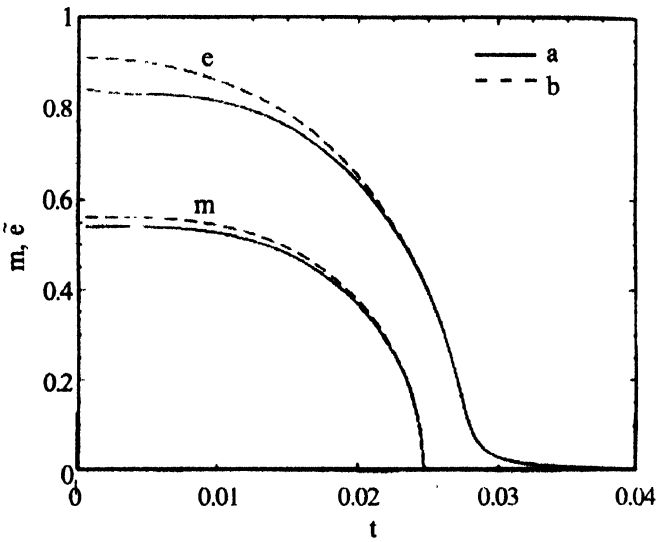

Figure 1. (a) Individual plots of m *vs* t with magnetic coupling $g_1 = 0.185$ and $\tilde{e}$ *vs* t with J-T coupling $g = 0.074$ for fixed values of $d = -0.005$, $v = 0.02$ respectively, (b) self-consistent plots.

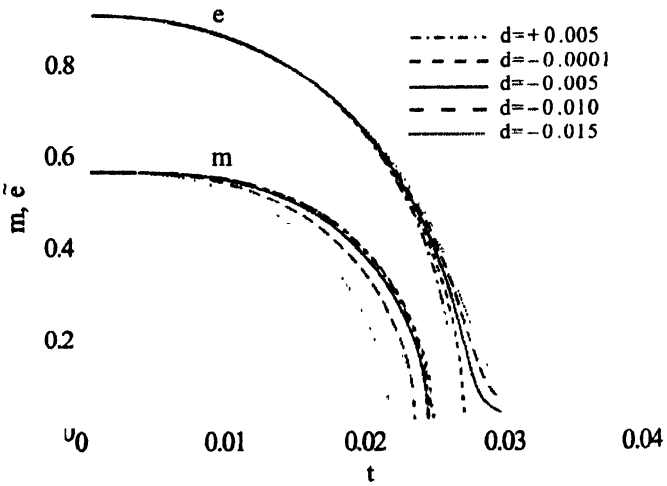

Figure 2. Self-consistent plots of m *vs* t and $\tilde{e}$ *vs.* t for fixed values of $v = 0.02$, $g_1 = 0.185$, $g = 0.074$ and for different values of $d = +0.005$, -0.0001, -0.005, -0.01, -0.015.

lattice strain ($\tilde{e}$) in eqn. (14) and the chemical potential (z) in eqn. (15) are solved self-consistently for a set of parameters under the half-filling band situation as shown in Figures 1 to 3 and the results with chemical potential variation are shown in Figures 4 and 5.

The temperature variation of the magnetization (m) and

elastic strain ($\tilde{e}$) are shown in Figure 1 in absence of magnetic field and chemical potential. The magnetic coupling strength is kept constant at $g_1 = 0.185$ in order to give a transition temperature $t_c = 0.0245$ corresponding to Curie temperature $T_c = 245$ K. Similarly the lattice coupling

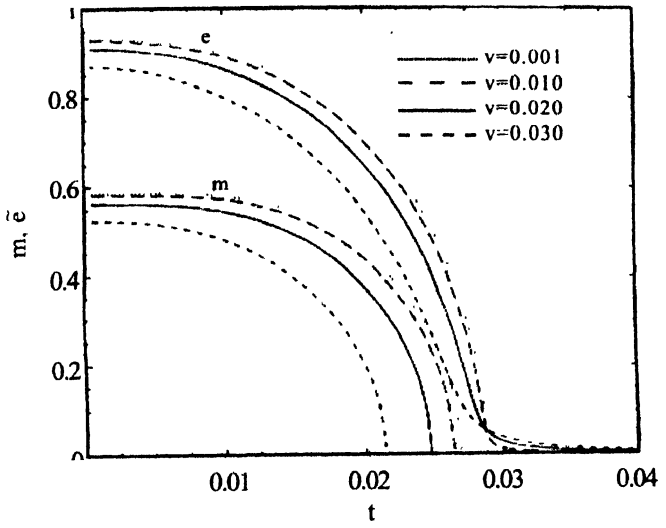

Figure 3. Self-consistent plots of m *vs* t and $\tilde{e}$ *vs.* t for fixed values of $d = -0.005$, $g_1 = 0.185$, $g = 0.074$ and for different values of $v = 0.001$, 0.01, 0.02, 0.03.

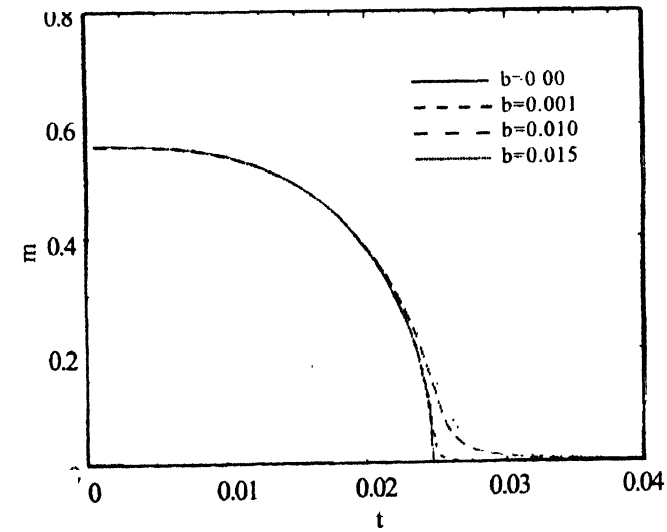

Figure 4. Self-consistent plots of m *vs* t for fixed values of $d = -0.005$, $v = 0.02$, $g_1 = 0.185$, $g = 0.074$, $x = 0.05$ and for different values of magnetic field $b = 0$, 0.001, 0.01, 0.015.

strength $g = 0.074$ gives a lattice distortion temperature $t_d = 0.0285$ corresponding to a distortion temperature $T_d = 285$ K, transition being continuous due to the presence of the hybridization between e_g and t_{2g} electrons. Initially $t_c < t_d$ before interplay (continuous line in Figure 1). The self-consistent plots of $m \sim t$ and $\tilde{e} \sim t$ are shown in Figure 1 (dotted curves). There is no change of transition temperatures t_c and t_d after interplay. However, both m and $\tilde{e}$ are enhanced as the temperature is reduced towards 0 K. The effect of the position of the t_{2g} electron level (d) on $m \sim t$ and $\tilde{e} \sim t$ is shown in Figure 2. Position of the t_{2g} electron level (d) with respect to Fermi level ($E_F = 0$) is positive (lying above) and negative (lying below). As the d-level approaches Fermi level from below (from d = 0.015 to 0.0001), the lattice strain is suppressed near the transition. The continuous transition of $\tilde{e}$ becomes sharp accompanied by a reduction in the distortion transition temperature t_d. Simultaneously the Curie temperature t_c is enhanced to a higher temperature accompanied by a corresponding enhancement of the magnetization (m) near the transition temperature.

The modulations of e_g electrons and t_{2g} states has a great bearing on the temperature dependence of magnetization (m) and strain ($\tilde{e}$) as shown in the Figure 3. For the low value of hybridization ($v = 0.001$ the transition temperature t_c and t_d are sharp and robust. As the hybridization (v) increases the strain is suppressed throughout the temperature range and the lattice distortion temperature becomes gradual as shown by the tail in $\tilde{e}$. The magnetization (m) is also suppressed throughout the temperature range with increase of the hybridization. Simultaneously the Curie temperature t_c is also suppressed but with a sharp transition from the paramagnetic to the ferromagnetic phase.

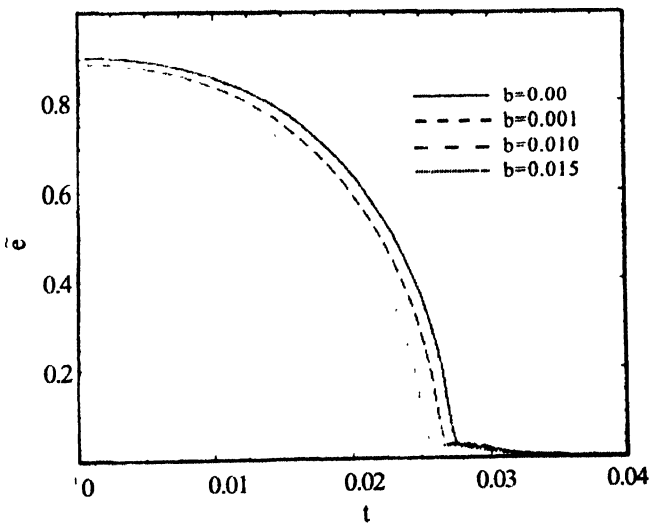

Figure 5. Self-consistent plots of $\tilde{e}$ *vs* t for fixed values of $d = -0.005$, $v = 0.02$, $g_1 = 0.185$, $g = 0.074$, $x = 0.05$ and for different values of magnetic field $b = 0$, 0.001, 0.01, 0.015.

The system stabilizes with a low doping concentration of 5% (not shown in Figure). The effect of external magnetic field on the magnetization and the strain in presence of doping concentration of $x = 0.05$ is shown in the Figures 4 and 5.

The increase of magnetic field (b) enhances the magnetization (m) only near the Curie temperature t_c (Figure 4). It also enhances t_c, but, as expected, the ferromagnetic to paramagnetic phase transition is gradual with increase of external field. A simple mean-field model [18] and the dynamic mean-field theory of Millis *et al* [13] show the similar behaviour of magnetization (m) with increase of external field (b) in presence of an effective J-T coupling.

The effect of external magnetic field (b) on the lattice strain ($\bar{e}$) is shown in the Figure 5. The increase of the magnetic field (b) suppresses the lattice strain ($\bar{e}$) in presence of a low doping concentration of 5%. It also suppresses the distortion temperature t_d.

5. Conclusion

We have considered a degenerate e_g band with a static J-T distortion present in it and the ferro-magnetism due to the t_{2g} electrons. The temperature dependence of magnetization (m) and lattice distortion ($\bar{e}$) are calculated self-consistently by varying different model parameters of the system. The position of the t_{2g} level (as it approaches the Fermi level) suppresses Curie temperature t_c but enhances the distortion temperature gradually. The magnetization and strain near the transition temperatures are sensitive to the position of t_{2g} level. The increase of the hybridization between e_g and t_{2g} bands suppresses m and $\bar{e}$ considerably. The increase of magnetic field pushes the Curie temperature to higher temperatures accompanied by a gradual transition as shown by theoretical studies [10–13]. It is seen that the strain is suppressed with increase of magnetic field. A low level of impurity stabilizes the system.

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